A STUDY OF THE HYDROLYSIS OF BROMOPENTAMMINE-CHROMIUM (III) BROMIDE IN ACETATE BUFFER

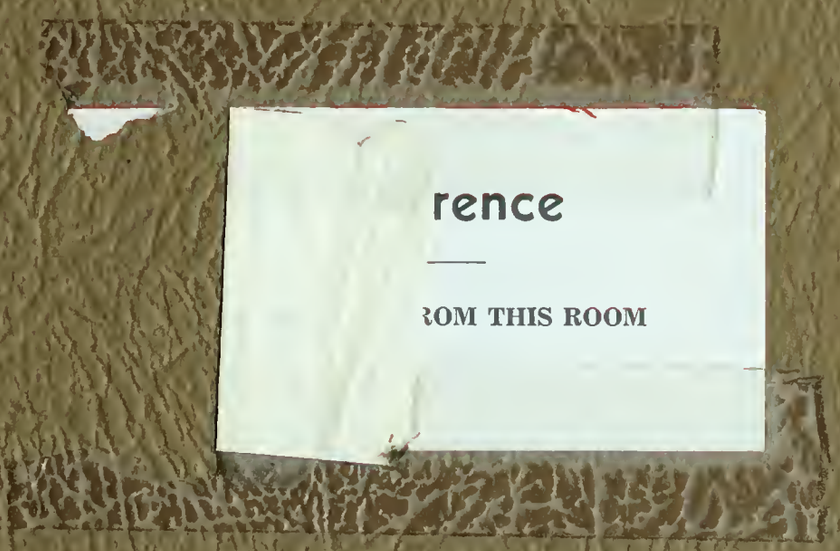
by

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B. Sc.

1959

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A STUDY OF THE HYDROLYSIS OF BROMOPENTAMMINE-CHROMIUM (III) BROMIDE IN ACETATE BUFFER

A DISSERTATION

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

by

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Edmonton, Alberta

September, 1959

UNIVERSITY OF ALBERTA

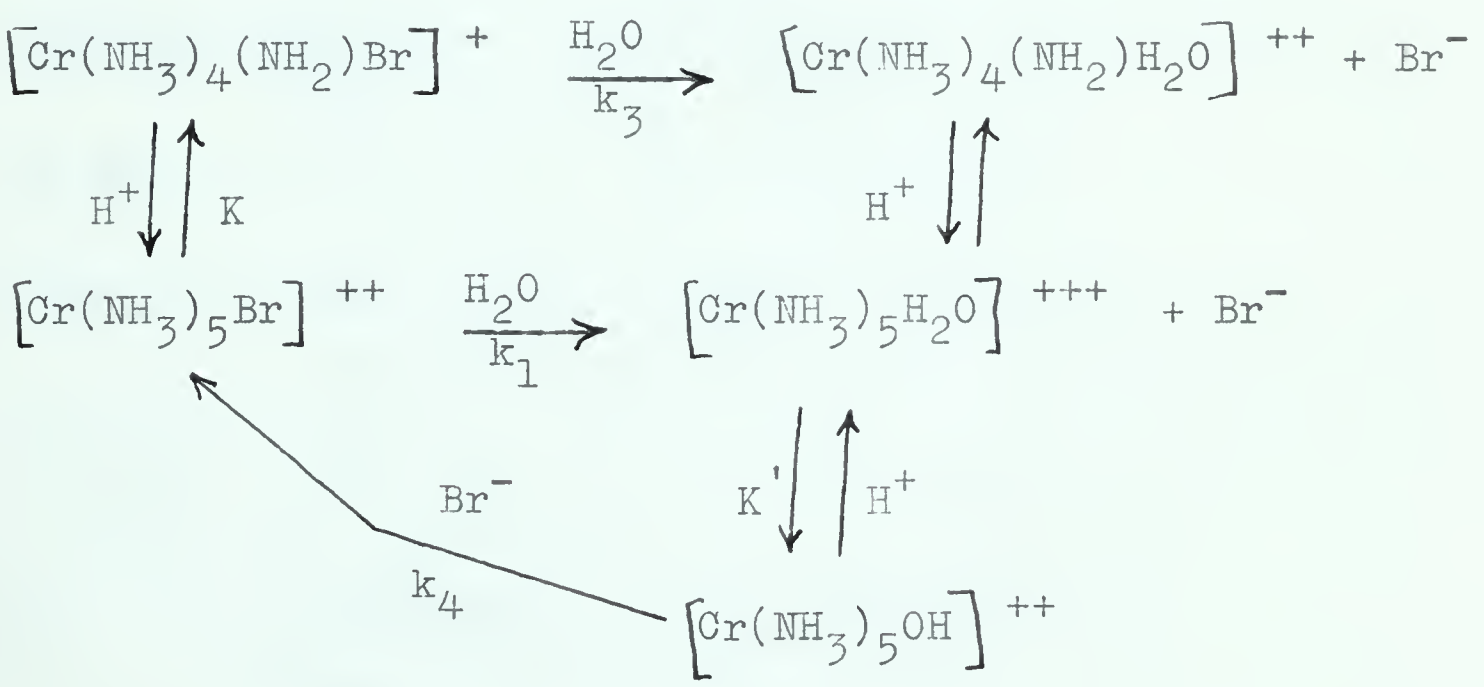
FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "A Study of the Hydrolysis of Bromopentamminechromium (III) Bromide in Acetate Buffer", submitted by Marilyn Ann Hayes in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The rate of the hydrolysis of bromopentammine-chromium (III) bromide was studied as a function of pH and of temperature, with various electrolytes. The observed first order rate constants were found to increase linearly with pH. The logarithm of the rate constant varied linearly with the reciprocal of the absolute temperature. A decrease in the rate constant was observed when the solution contained an excess of bromide ion at 25°. An increase in the concentration of the acetate buffer solution used, resulted in a corresponding increase in the rate constant.

The following reaction scheme is proposed for the hydrolysis:





ACKNOWLEDGEMENT

The author wishes to thank Dr. W. E. Harris and Dr. W. J. Wallace, with whose enthusiastic guidance this work was carried out.

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A STUDY OF THE HYDROLYSIS OF BROMOPENTAMMINECHROMIUM (III) BROMIDE IN ACETATE BUFFER

INTRODUCTION

In recent years the kinetics of substitution reactions of metal complexes have been intensively studied as an aid in the elucidation of the factors which are important in the solution chemistry of inorganic compounds. Since numerous cobalt complexes can be prepared and since their substitution reactions are slow enough to be studied by conventional methods, these compounds have been studied in greater detail than any others[1]. It is thought generally that reactions in aqueous solution involve an aquo intermediate[2] as indicated in equations (1) and (2) for the chloropentamminecobalt (III) ion

$$\left[Co(NH_3)_5Cl\right]^{++} + H_2O \longrightarrow \left[Co(NH_3)_5\ H_2O\right]^{+++} + Cl^- \qquad (1)$$

$$\left[Co(NH_3)_5\ H_2O\right]^{+++} + Y^- \longrightarrow \left[Co(NH_3)_5\ Y\right]^{++} + H_2O \qquad (2)$$

The product of reaction (1) is both slow to react with other ions and is also thermodynamically stable with respect to substitution in water solution. Hence the hydrolysis reaction, equation (1), has been most studied.

Studies with cobalt complexes made in aqueous solution yield a linear plot for the log of the concentration of complex vs. time. This result is to be expected, even if the attack of water is part of the rate determining step,

since the concentration of the water does not change during the reaction. The hydrolysis rate therefore depends only upon the concentration of the complex and is first order or pseudo first order. This observation alone furnishes little information about the mechanism of the reaction. Nevertheless, the way in which the rate constant is affected by various changes in the nature of the reactants and conditions of reaction is useful in giving some insight into the mechanism of substitution reactions.

Substitution reactions can be divided into two main types with regard to mechanism[3]. In one type, S_N1, the entering group does not participate in the rate determining step, while in the other type, S_N2, the entering group does participate in the rate determining step. In reactions proceeding by an S_N1 mechanism, the rupture of the cobalt-ligand bond is rate determining, whereas those proceeding by a limiting S_N2 mechanism, the formation of the new bond is rate determining. Consequently, the rate of an S_N1 reaction ought to be dependent upon the group being displaced while the rate of an S_N2 limiting reaction ought to be independent of the displaced group.

If the displacing group enters the molecule from the side opposite to that occupied by the displaced group, it would be expected that steric crowding on the back side of the molecule would lead to a reduced rate of reaction. On this basis bis-ethylenediaminecobalt (III) complexes

would be expected to react more slowly by rearward attack than would the corresponding cobalt (III) ammonia complexes. However, these complexes react only slightly more slowly than non-chelated complexes[4], and hence this would be an argument against an S_N2 trans attack in this example. Similarly, increased alkyl substitution on the carbon or nitrogen of the ethylenediamine, with its accompanying increased steric crowding of the complex provides further opportunity for the investigation of either cis or trans S_N2 attack. These studies indicate that substitution of a single methyl group on the nitrogen has no significant effect but when substitution is carried further, there is a corresponding increase in the rate constant[5]. Certainly, increasing the crowding about the cobalt atom would not be conducive to an S_N2 mechanism in which an increase in coordination number to seven is required. On the other hand, such an increase in the size of the inert ligands is expected to favour an S_N1 mechanism in which the coordination number decreases to five. Hence, the acceleration in rate upon increased substitution is strongly suggestive of a dissociation (S_N1) mechanism.

So far, only the use of rates in the elucidation of the mechanism of hydrolysis of cobalt (III) complexes has been described. The use of activation energies in conjunction with the rates are a more reliable guide than rates alone in attempting to assign a mechanism to a particular displacement reaction[6]. The experimental activation energies

for the hydrolysis of various cobalt (III) complexes are found to be in the range of 20-30 kcal[7]. On the basis of crystal field theory[8], approximate activation energies for the displacement or dissociation mechanisms can be calculated[9]. According to this theory, all the d orbitals in a free gaseous metal ion are equal in energy. Under the influence of the fields associated with attached ligands the d levels will become unequal in energy. In particular those orbitals lying in the direction of the ligands are raised in energy with respect to those lying away from the ligands. By preferentially filling the low energy orbitals, the d electrons can stabilize the system compared to random filling of the orbitals. The gain in energy obtained in this way is called the crystal field stabilization energy. An octahedral arrangement of ligands will produce two very high energy orbitals, d_{z^2} and $d_{(x^2-y^2)}$, and three low energy orbitals. The six d electrons of trivalent cobalt, will fit in the three low energy orbitals of an octahedral complex and as a consequence cobalt (III) complexes are found to be crystal field stabilized. In an S_N2 displacement involving an octahedral complex the transition state would involve a seven coordinated intermediate which would force ligands closer to these high energy orbitals and hence would lower the crystal field stabilization energy. The activation energies for such intermediates have been estimated from this loss in crystal field stabilization energy to be 103 kcal[10],

which is considerably greater than the 20-30 kcal observed. On the other hand, with an S_N1 displacement involving an octahedral complex either a trigonal bipyramid or a square pyramid are possible for the intermediate with coordination number five. The trigonal bipyramid with an estimated activation energy of 121 kcal[10] is even less stable than the seven coordinated intermediate. However, on forming an unrearranged square pyramid, the loss in stabilization energy, due to the removal of one ligand would be considerably less. The predicted activation energy in this case is 6-94 kcal[10]. The range in this value represents limits for the extreme cases where the vacated position in the coordination sphere is occupied by the water or where it is left completely vacant. Consequently, this is the only one of the suggested intermediates which can be consistent with the experimental activation energies.

In summary, the evidence discussed above seems to indicate that cobalt displacement reactions are predominately S_N1 in character.

Those displacement reactions with chromium complexes which have been studied, are similar to those of cobalt in following first order kinetics. Hamm and Schull[11] made a study of the kinetics of the hydrolysis of dichlorotetraquochromium (III) chloride to the monochloropentaquo species in aqueous solution.

$$\left[Cr(H_2O)_4Cl_2\right]^+ + H_2O \longrightarrow \left[Cr(H_2O)_5Cl\right]^{++} + Cl^- \qquad (3)$$

The hydrolysis was found to be first order with respect to chromium ion concentration, first order with respect to the reciprocal of the hydrogen ion concentration, and independent of the chloride ion concentration. The rate equation proposed which fitted these observations, is given in equation (4) and the mechanism is illustrated in equation (5).

$$\frac{d\left[Cr_t\right]}{dt} = \frac{-k\left[Cr_t\right]K}{\left[H^+\right]} = -k'\left[Cr_t\right] \qquad (4)$$

Cr_t is the total concentration of chromium in the two forms in equilibrium on the left in equation (5), K is the equilibrium constant, k is the rate constant for the exchange, and $k' = \frac{kK}{\left[H^+\right]}$.

$$\begin{array}{ccc} \left[Cr(H_2O)_4Cl_2\right]^+ & & \left[Cr(H_2O)_5Cl\right]^{++} \\ K \downarrow \uparrow H^+ & & \downarrow \uparrow H^+ \\ \left[Cr(H_2O)_3Cl_2(OH)\right] + H_2O & \xrightarrow{k} & \left[Cr(H_2O)_4Cl(OH)\right]^+ \end{array} \qquad (5)$$

The mechanism proposed by Hamm and Schull is analogous to the S_N1 CB (S_N1 conjugate base) mechanism discussed by Pearson, Meeker and Basolo[12], for the base hydrolysis of the chloropentamminecobalt (III) ion. The extraction of a hydrogen ion, increases the electron density on the chromium and this would reduce the strength of the Cr-Cl bond. Hence a unimolecular bond rupture occurs more easily. On the evidence that no significant change in the rate was found,

upon changing the ionic strength of the solution, it was proposed that the direct reaction, shown in equation (3), does not occur[11]. The above reasoning, leading to this conclusion that the uncharged dichlorohydroxo complex was the only rate determining species in solution, is not obvious.

Since the chemistry of chromium (III) in aqueous solutions is complicated by olation[13], it is possible that such reactions could contribute to the removal of chloride from the complexes as shown in equation (6). The rates of these reactions are pH dependent

$$2\left[Cr(H_2O)_3Cl_2(OH)\right] \longrightarrow (H_2O)_3\text{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Cr}}\text{-}O\text{-}\underset{\underset{OH}{|}}{\overset{\overset{Cl}{|}}{Cr}}\text{-}(H_2O)_3 + HCl \qquad (6)$$

Consequently, a study of a series of complex ions in which all the coordination positions, except the one which is of interest, are blocked, would eliminate this complication. This specification is met by the halogenopentamminechromium (III) complex salts. However, there have been few studies of this type of chromium complex.

The only value in the literature for the rate constant for the reaction,

$$\left[Cr(NH_3)_5Br\right]^{++} + H_2O \longrightarrow \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^- \qquad (7)$$

was determined by Freundlich and Bartels[14] in 1922. The reaction was found to be first order in chromium with a rate constant 3×10^{-3} min^{-1}.

Most kinetic studies of chromium complexes have been made by various spectrophotometric methods. However, in the halogenopentamminechromium (III) series, the wave lengths of maximum extinction of the halogenopentammine-chromium (III) ion and of the aquopentamminechromium (III) ion lie too close together for easy analysis, as can be seen from Figure 1. Another disadvantage of the spectrophoto-metric method is that the extinction coefficients of both compounds have to be known. Simultaneous equations have to be solved in analyzing the results and consequently this makes the method tedious. Therefore it was decided to attempt a polarographic approach. With only two species in solution, only one of the half wave potentials has to be known, and no simultaneous equations have to be solved. A polarographic technique will be successful when the difference in the half wave potentials of the reactant and product is of the order of 0.1-0.2 volts.

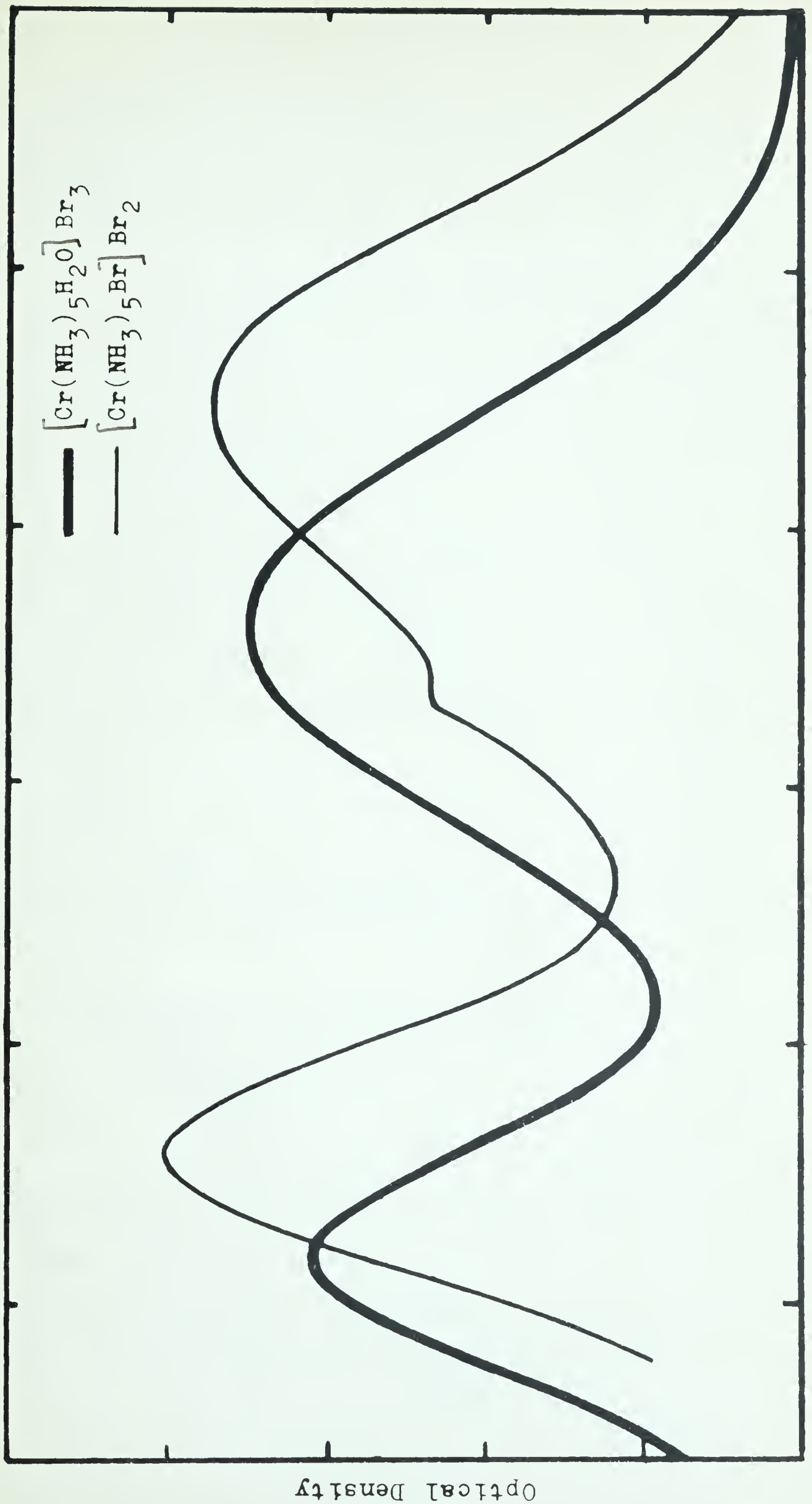


Figure 1 - Spectra of $[Cr(NH_3)_5H_2O]Br_3$ and of $[Cr(NH_3)_5Br_2]Br_2$ in 0.9 M perchloric acid. (From T. P. Jones, private communication)

EXPERIMENTAL

A. Preparation of Compounds

1. Aquopentamminechromium(III) Ammonium Nitrate

$$\left[Cr(NH_3)_5H_2O\right](NO_3)_3 \cdot NH_4NO_3$$

This salt was prepared according to M. Mori[15]. Potassium chromium (III) sulfate twelve hydrate was reacted with aqueous ammonia and ammonium nitrate at about 60°. The mixture was cooled to about 20°, air was passed through the solution to remove excess ammonia, and an excess of concentrated nitric acid was added. Precautions were taken to keep the temperature of the solution below 30° during the nitric acid addition. The resulting orange crystals were purified by recrystallization from a solution of ammonium nitrate.

Analysis

Calculated for $\left[Cr(NH_3)_5H_2O\right](NO_3)_3 \cdot NH_4NO_3$	Found
Cr 12.3%	Cr 12.3%

2. Bromopentamminechromium(III)Bromide

$$\left[Cr(NH_3)_5Br\right]Br_2$$

A procedure devised by M. Mori[16] was used. Aquopentamminechromium (III) ammonium nitrate was dissolved in a dilute ammoniacal solution and reacted with an excess of 48% hydrobromic acid to give aquopentamminechromium (III) bromide. The crystals which precipitated were digested on a steam bath

with 48% hydrobromic acid to produce bromopentamminechromium (III) bromide.

Analysis

Calculated for $\left[Cr(NH_3)_5Br\right] Br_2$		Found	
Cr	13.8%	Cr	13.8%
NH_3	22.6%	NH_3	22.4%
Br	63.6%	Br	63.2%

3. Chloropentamminechromium (III) Chloride

$\left[Cr(NH_3)_5Cl\right] Cl_2$

The procedure described below is a modification of that used for the preparation of bromopentamminechromium (III) bromide[16]. Forty-two grams of aquopentamminechromium (III) ammonium nitrate was dissolved in a mixture of 60 ml. of water and 20 ml. of 15 M aqueous ammonia. To this solution were added, 130 ml. of 37% hydrochloric acid and 100 ml. of 95% ethanol, and the mixture was cooled to 0°. The orange precipitate which formed was collected on a filter and washed with 95% ethanol. The washed solid was slurried with 300 ml. of water, treated with 260 ml. of concentrated hydrochloric acid, stirred for 10-15 minutes and then cooled to 0°. The solid aquopentamminechromium (III) chloride was removed by filtration and washed with 95% ethanol. The yield was 16.6 grams (64%).

The aquopentamminechromium (III) chloride crystals were added to 200 ml. of water and 65 ml. of concentrated

hydrochloric acid was then added. The mixture was digested with stirring for 45 minutes while three 65 ml. portions of concentrated hydrochloric acid were added at intervals of several minutes. After cooling to 15°, the precipitate of chloropentamminechromium (III) chloride was filtered and then washed with 95% ethanol and air dried. The yield was 13.6 grams, (53% based on the double nitrate).

Analysis

Calculated for $\left[Cr(NH_3)_5Cl\right] Cl_2$		Found	
Cr	21.4%	Cr	21.1%
NH_3	35.0%	NH_3	34.1%
Cl	43.7%	Cl	43.7%

4. Iodopentamminechromium (III) Iodide $\left[Cr(NH_3)_5I\right] I_2$

A similar procedure[16] was followed in an attempt to prepare the corresponding iodo complex but this was unsuccessful. Three different products resulted from three attempts, one flamingo colored, one mauve and one rust colored. The compositions found for these compounds are given in Table I.

TABLE I

Relative Compositions of the Three Products from the Attempted Preparations of Iodopentamminechromium (III) Iodide

	Cr	NH_3	I
flamingo compound	1	5.3	2.9
mauve compound	1	5.5	2.5
rust compound	1	3.9	2.1

B. Analytical Methods

1. Chromium Analysis

The method used was based upon that given by Vogel[17].

A sample of about one third of a gram of the chromium ammine was dissolved in about 130 ml. of 0.2 N sulfuric acid. Enough silver nitrate was added to precipitate the halide when present, and then a few ml. excess was added. One to two grams of ammonium persulfate was added and the solution was boiled for about twenty minutes. After cooling the solution was decanted, and the residual silver halide washed by decantation. To the combined solution and washings 5-10 grams disodium phosphate and a few drops of sodium diphenylamine sulfonate indicator were added. A measured excess of standard iron (II) sulfate solution was then added and this was back titrated with standard potassium dichromate.

2. Halogen Analysis

In halogenopentamminechromium (III) halides one halogen is inert while the remaining two are labile. To determine labile halogen a sample of the chromium ammine halide, weighing about 0.1 gram was dissolved in 200 ml. of water and titrated conductometrically with standard 0.1 N silver nitrate. The total halogen content was determined by titrating a similar solution, after it had been heated to boiling to hydrolyze the inert halogen. The labile halogen

value was then subtracted from the total halogen value to give the amount of inert halogen.

The circuit used for the conductometric titration was that of Sand and Griffins[18].

3. Ammonia Analysis

A 0.5-1.0 gram sample of the complex was dissolved in 300 ml. of water. Boiling chips and 200 ml. of 10% sodium hydroxide were then added. The solution was heated to boiling and the ammonia liberated was distilled into 150 ml. of standard 0.2 N hydrochloric acid. The acid solution was then back titrated with standard sodium hydroxide using methyl red as an indicator.

C. Apparatus

Polarograms were recorded on a Leeds and Northrup Electrochemograph type E at 25° or at 0°. Potentials were measured relative to the saturated calomel electrode (SCE). The capillary had the following characteristics:

$$m^{2/3}\ t^{1/6} = 3.29\ mg^{2/3}\ sec^{-1/2},$$

with a drop time 2.0 seconds and a 65 cm. head of mercury.

The constant temperature at 0.06° $\pm$ 0.05° was obtained with a mixture of ice and distilled water contained in a three litre cylindrical Dewar flask. The bath was insulated with a cover to minimize heat transfer.

The 25.0° ± 0.05° bath was thermostated by means of a mercury switch thermoregulator in conjunction with a Precision Scientific Co. thyratron tube relay Number 6532.

The thermostating in the 50.0° ± 0.03° bath operated with a Thermocap Relay from Niagara Electron Laboratories used with a Beckman thermometer.

The polarographic bath at 25° ± 0.5° was thermostated by means of a mercury switch thermoregulator in conjunction with a Fisher Transistor Relay.

All temperatures were checked with National Bureau of Standards thermometer.

D. Buffer Solutions

Acetate buffers at pH 3.7, 4.7 and 5.7 were made 0.1 M in sodium acetate and one at pH 2.7 was made 0.01 M in sodium acetate. A chloroacetate buffer at pH 2.0 was made 0.1 M in chloroacetate ion and a formate buffer was made 0.1 M in sodium formate. These buffers were all standardized with a pH meter at 25° against a reference acetate buffer at pH 4.7. The reference buffer, 0.1 M in sodium acetate, was made up by volume, from carbonate free sodium hydroxide which had been standardized against potassium acid phthalate with phenolphthalein, and acetic acid which had been standardized against the sodium hydroxide. Reagent grade chemicals were used throughtout.

The pH of the buffers were determined at room temperature, but since the acetate buffers were used over a

50° temperature range, corrections had to be made in the pH values, due to the variation in the dissociation constant of the acetic acid with temperature. The pK values of acetic acid, determined by Noyes[19] for a temperature range of 18°-306°, were plotted against the reciprocal of the absolute temperature. From this plot, shown in Figure 2, the pK values at 0°, 25° and 50° were found to be 4.73, 4.74 and 4.78 respectively. The pH of the various buffers were then calculated by multiplying these values by the salt to acid ratio.

E. Determination of Rate Constants

One hundred ml. of acetate buffer solution was brought to the desired temperature and purged with nitrogen for 5-10 minutes. Enough complex was added to make an approximately 0.001 M solution; the mixture was stirred until all the complex had dissolved (about five minutes) and then the container was quickly immersed in a constant temperature bath. In the case of runs made at 25°, ten ml. aliquots of the solutions were periodically transferred to a polarographic cell[20]. Four drops of 0.1% thymol solution were added to suppress the maxima and the solution was purged with nitrogen for 5-10 minutes to remove oxygen prior to running the polarograms. For runs made at 50°, ten ml. aliquots of the solution were pipetted with a cold pipette into a cold polarographic cell and this was then quickly put into an

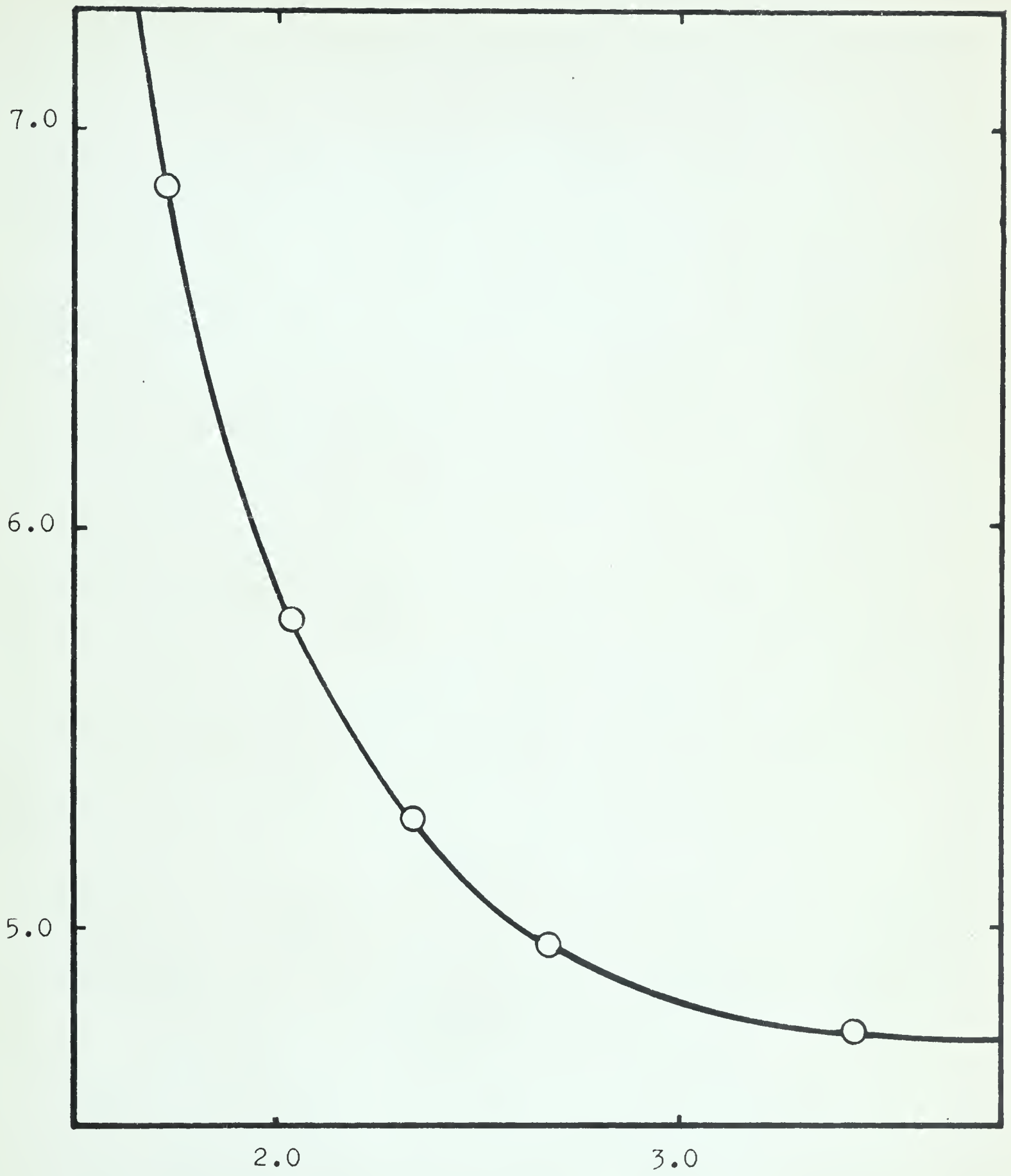


Figure 2 - Variation of Dissociation Constant, K, with Temperature[19]

icebox to quench the reaction. These were later immersed in the polarographic constant temperature bath at 25°, purged with nitrogen for five minutes and polarograms were run immediately. In runs made at 0°, the polarograms were recorded at 0°, after 4 drops of thymol solution had been added and the solution had been purged with nitrogen.

Relative amounts of unhydrolyzed and hydrolyzed chromium ammine were determined from the polarograms. Polarograms of one millimolar bromopentamminechromium (III) bromide in acetate buffers of pH 2.7, 3.7, 4.7 and 5.7 consisted of two waves for the reduction of trivalent chromium to the divalent state. The height of the first wave decreased with time and the height of the second increased correspondingly. Figure 3 shows polarograms of one millimolar bromopentamminechromium bromide in 0.1 M acetate buffer of pH 4.7, and the half-wave potentials observed for the two waves are shown in Table II.

TABLE II

Half-Wave Potentials Observed in Polarograms of Bromopentamminechromium (III) Bromide in Acetate Buffer Solutions Containing 0.002% Thymol

pH	2.7	3.7	4.7	5.7
$E_{1/2}$ first wave volts vs. S.C.E.	-0.58	-0.61	-0.62	-0.67
$E_{1/2}$ second wave volts vs. S.C.E.	-0.80	-0.83	-0.83	-0.89

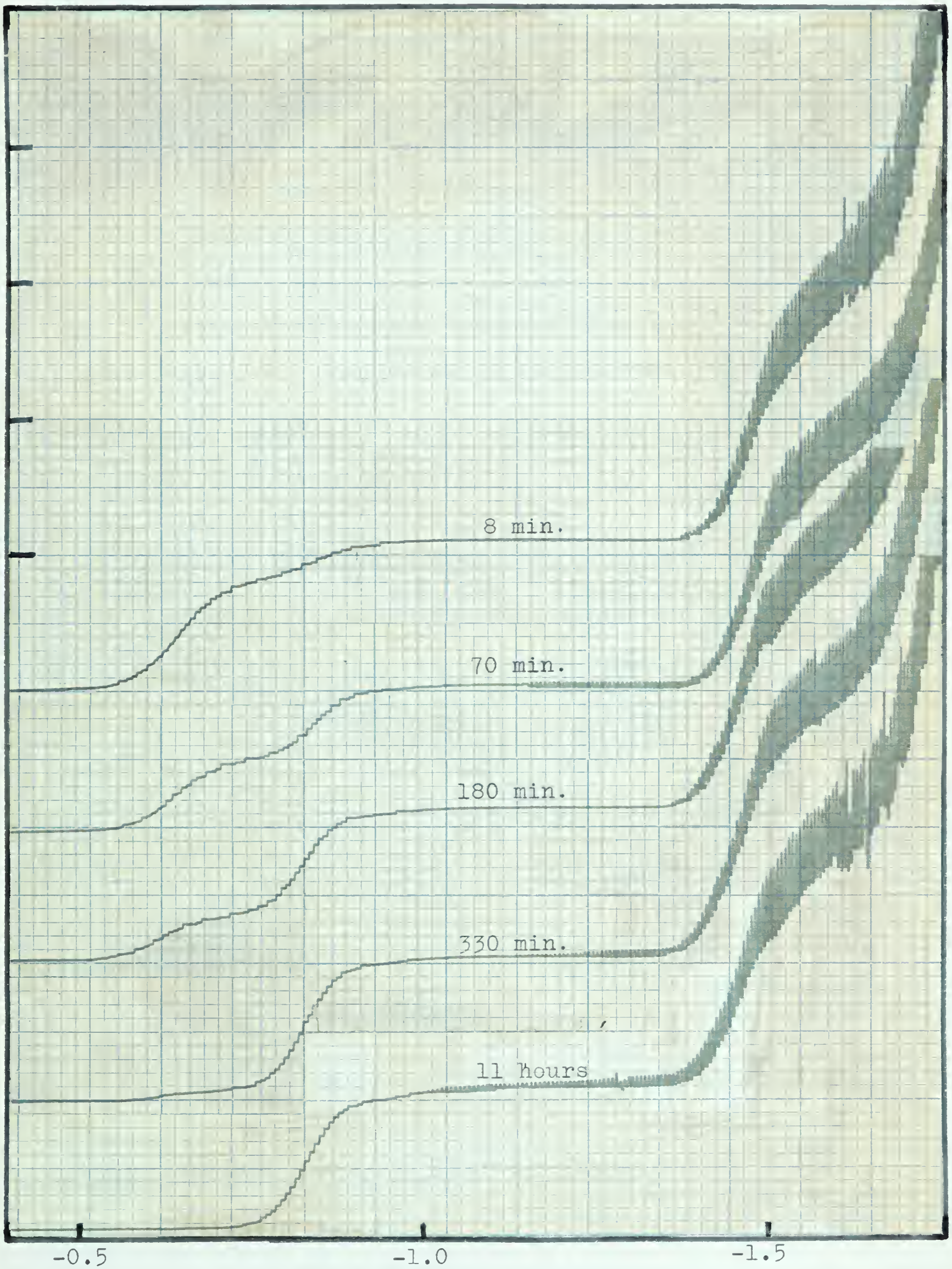


Figure 3 - Polarograms of one millimolar $\left[Cr(NH_3)_5Br\right]Br_2$ in acetate buffer solution pH 4.7 at 25°.

The half-wave potentials at all the pH values tended to become slightly (0.01-0.02 volts) more positive during the first hour in runs at 25° and then remained constant for the next five to six hours. The values recorded in Table II are those determined after they had become constant.

Polarographic waves taken at 25°, at pH 3.7 and 4.7 were tested for reversibility, by plotting log $\frac{i}{i_d - i}$ vs. potential, where i_d is the diffusion current and i is the current at any potential. The slopes of these plots for the first wave, at pH 3.7 and 4.7 were found to be 0.76 volts and 0.72 volts, and for the second wave 0.62 volts. This indicates that the reduction of the bromopentammine (first wave) is irreversible while the reduction of the aquopentammine (second wave) is reversible. This result is understandable when it is considered that the reduction of bromopentamminechromium (III) to bromopentamminechromium (II) will lead to rapid hydrolysis of the chromium (II) complex, as a result of going from a metal species which is crystal field stabilized to one which is not.

Polarograms of aquopentamminechromium (III) bromide in the various buffer solutions gave only one wave whose half-wave potential (-0.80 to -0.89 v vs. S.C.E.) corresponded to that of the second wave (see Table II) in the bromopentamminechromium (III) series. Consequently, it was thought that the first wave, $E_{1/2}$ = -0.58 to -0.67v was due to

the reduction of the bromopentamminechromium (III) ion while that of the second wave ($E_{\frac{1}{2}}$ = -0.80 to -0.89v) was due to the reduction of the aquopentamminechromium (III) ion. This would seem to be a reasonable assumption when it is remembered that the water molecule has a greater electron donating tendency than the bromide ion. Hence the chromium in the aquo complex would be expected to be harder to reduce than the chromium in the bromo complex, and hence a more negative potential would be required. This reasoning is supported by the evidence found by Hamm and Schull[11] in the transition from the dichlorotetraquochromium (III) ion to the monochloropentaquo species and then to the hexaquo species. The half-wave potentials shift from -0.61v to -0.85v to -0.89v, illustrating the increasing difficulty of reducing the chromium with increased replacement of chloride with water. There is a relatively small difference between the half-wave potentials of the monochloropentaquo species and the hexaquo species. Both the hexammine and the aquopentammine have half-wave potentials which are nearly the same as the hexaquo[21]. Consequently it would be expected that the change in half-wave potentials from the aquopentammine to the chloropentammine would be approximately the same as the change from the hexaquo to the chloropentaquo. However, the shift brought about by replacing either ammonia or water with a bromide ion would be expected to be greater

than that caused by the replacement with chloride ion, because of the greater difference in electron donation between bromide and water as compared with chloride and water. The chloropentamminechromium (III) ion in the same buffer solutions, gave only one observable polarographic wave in this region. The half-wave potential, of -0.78 volts vs. S.C.E. in the buffer at pH 4.7, was only slightly more positive than that for the aquopentammine complex. Hence it is evident that the chloropentammine is reduced at a potential slightly more positive than the aquopentammine, as was predicted above. For this reason no kinetic studies could be made on the chloropentammine in these media, by a polarographic method, whereas it was possible to make kinetic studies of the bromopentammine because of the greater separation of half-wave potentials of the reactant and the product.

In a chloroacetate buffer solution of pH 2.0, the chloride complex and the bromide complex gave substantially more poorly defined polarographic waves, as can be seen in Figure 4.

At pH values greater than 5.7, extensive base hydrolysis leading to decomposition of the complex by loss of ammonia, and subsequent precipitation of chromium hydroxide, occurs too rapidly to allow study of the aquation reaction.

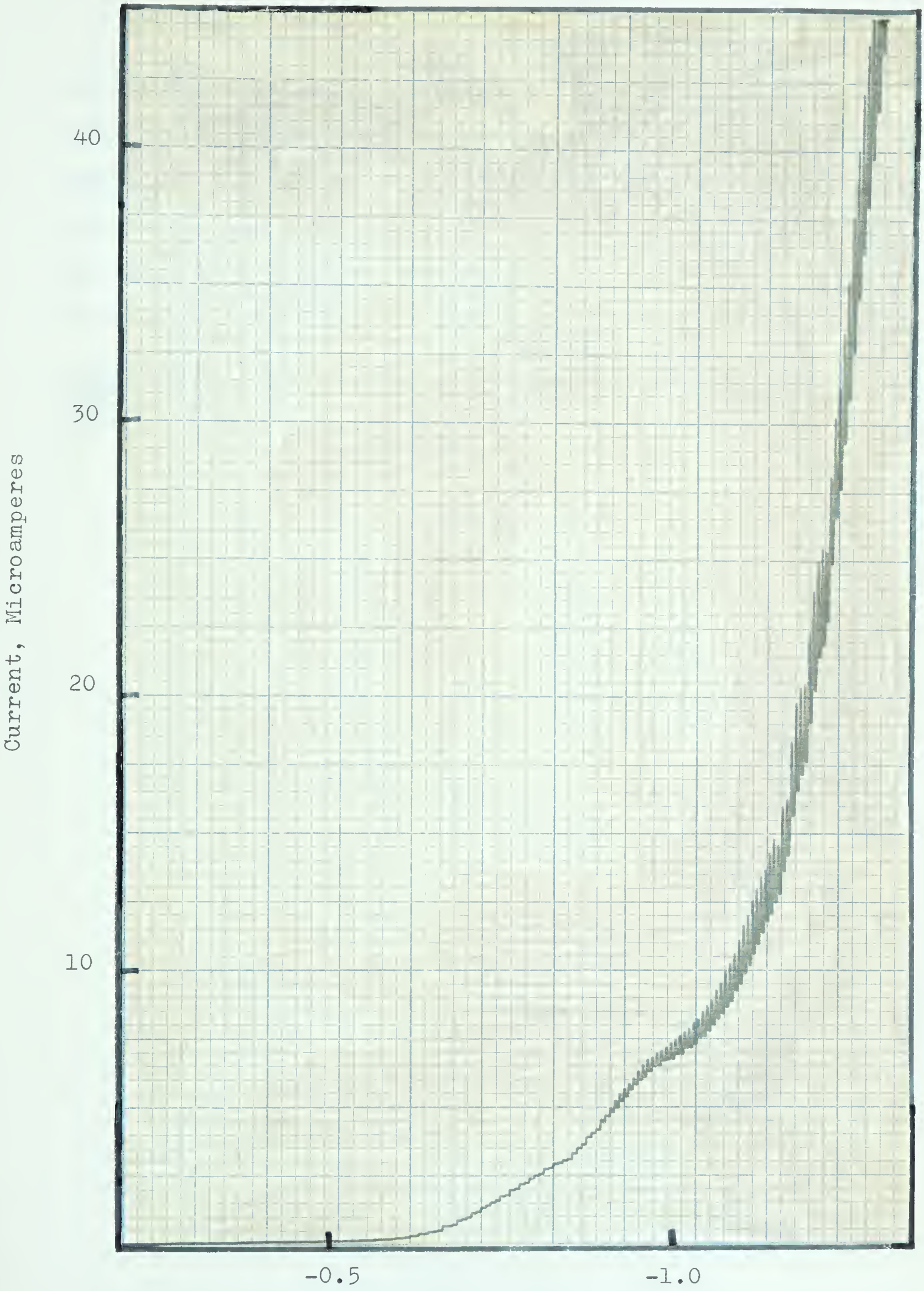


Figure 4 - Polarogram of $[Cr(NH_3)_5Br]\ Br_2$ in chloroacetate buffer solution pH 2.0

The decrease in the concentration of the bromopentamminechromium (III) ion was followed by reading the diffusion current at the inflection point between the two waves. The logarithm of the diffusion current was then plotted against time and the rate constant calculated from the slope of the plot. For example, in the plot for pH 5.7 in Figure 5, the slope is $\frac{(0.300 + 0.175)}{(250-110)}$ min^{-1} or $\frac{0.475}{140}$ min^{-1}. The observed rate constant is 2.303 times the slope or 7.81×10^{-3} min^{-1}.

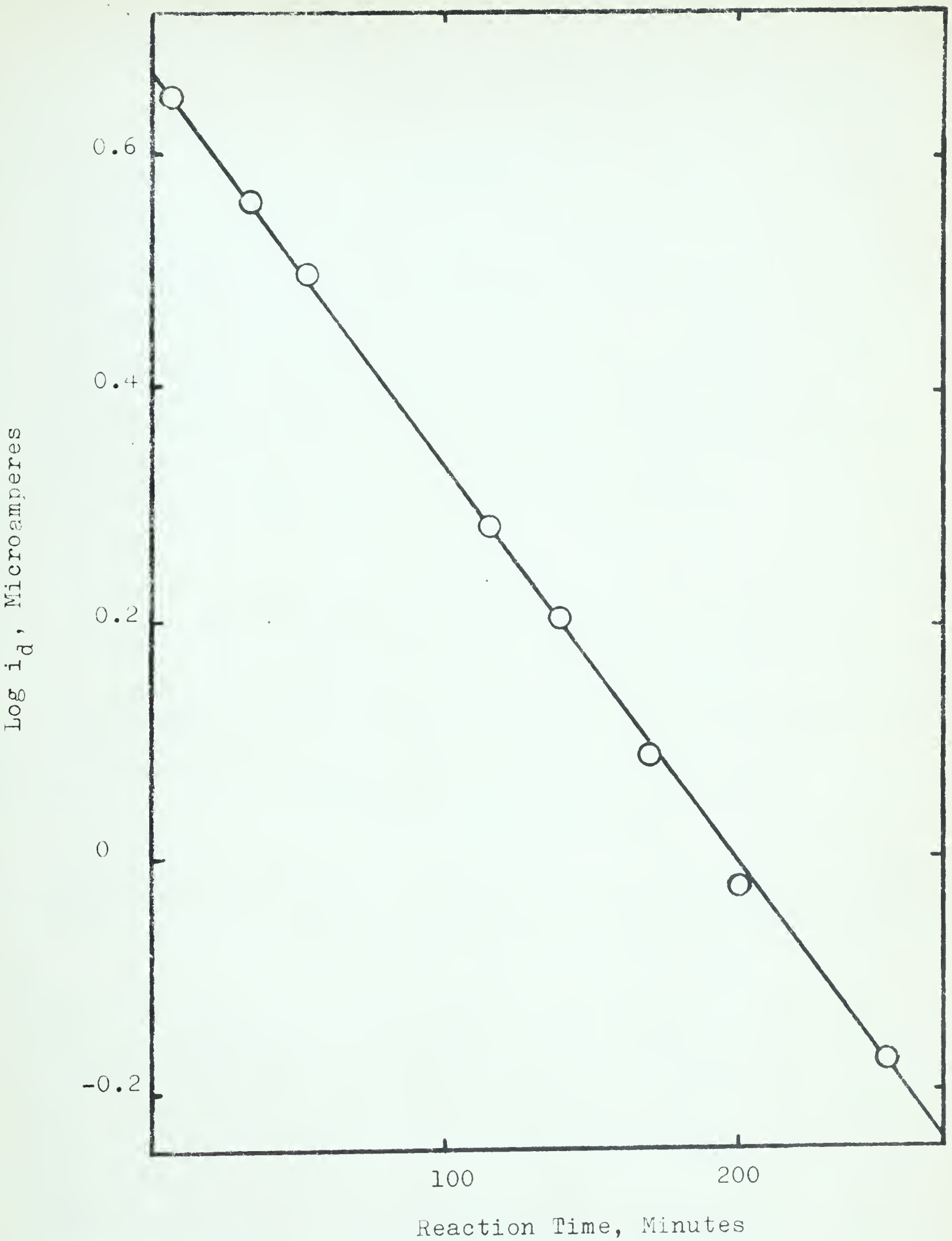


Figure 5 - Plot of the log of the diffusion current, in microamperes, of the first wave against the reaction time.

F. Experimental Results

The rate of hydrolysis of bromopentamminechromium (III) bromide was studied as a function of pH and of temperature, with various electrolytes. The hydrolysis reaction was found to be first order with respect to the concentration of the bromopentamminechromium (III) ion. Table III gives a list of the first order rate constants found at three temperatures, and four pH values. All buffer solutions were 0.1 M in acetate ion except the buffer at pH 2.7 which was 0.01 M in acetate ion.

TABLE III

First Order Rate Constants for the Reaction

$$\left[Cr(NH_3)_5Br\right]^{++} + H_2O \rightarrow \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^-$$

In Acetate Buffer Solutions Containing 0.002% Thymol

$\left[Cr(NH_3)_5Br\right]$ Br_2 Concentration 0.001 M

Rate Constants Min^{-1}

temp.	pH 2.7∓	pH 3.7	pH 4.7	pH 5.7
0°	2.04×10^{-4}	2.64×10^{-4}	2.76×10^{-4}	2.90×10^{-4}
25°	5.75×10^{-3}	6.48×10^{-3}	7.11×10^{-3}	7.60×10^{-3}
	5.50×10^{-3}	6.43×10^{-3}	7.08×10^{-3}	7.97×10^{-3}
		6.40×10^{-3}	7.19×10^{-3}	7.85×10^{-3}
				7.81×10^{-3}
50°*		8.65×10^{-2}	1.15×10^{-1}	1.19×10^{-1}
		8.69×10^{-2}	1.05×10^{-1}	1.02×10^{-1}

* polarograms recorded at 25° with no thymol

∓ acetate ion concentration of 0.01 M

The rate constants increase with temperature. The Arrhenius equation[22]

$$k = Ze^{-E_a/RT}$$

was used in determining the activation energies and frequency factors. In this equation, k is the rate constant, Z is the frequency factor, E_a is the activation energy, R is the gas constant, T is the absolute temperature, and e is the base of natural logarithms. Figure 6 gives plots of the logarithm of the rate constant vs. the reciprocal of the temperature, for the four pH values. The activation energies were calculated by multiplying the slopes of these plots by 2.303R. For example, in the plot at pH 3.7 the slope is $\frac{3.10-0.90}{3.560-3.060}$ or $\frac{2.20}{0.500}$ deg. The activation energy is then 2.303 X 1.987 X $\frac{2.20}{.500}$ or 20.14 kcal/mole. The frequency factors were then calculated using the expression $\log Z = \log k + \frac{E_a}{2.303RT}$.

For example, at pH 3.7, $\log Z = -0.90 + \frac{20.14 \text{ X } 3.060}{2.303 \text{ X } 1.987} = 12.57$.

Therefore $Z = 3.7 \text{ X } 10^{12}$. Table IV shows values of the activation energies and frequency factors calculated from these data, along with an estimate of the reliability of these values.

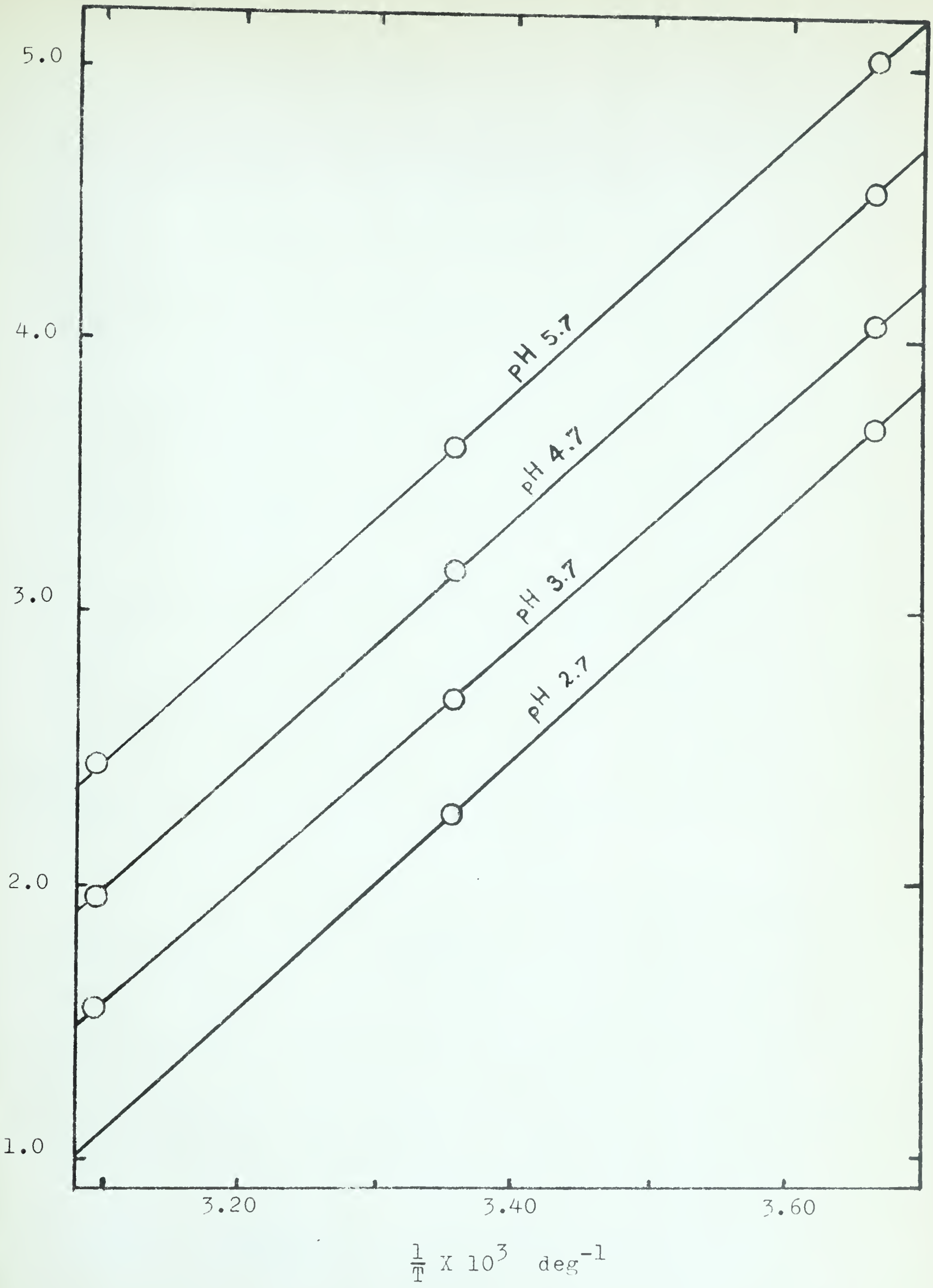


Figure 6 - Plot of the negative log of the observed rate constant against the reciprocal of the absolute temperature.

TABLE IV

Activation Energies and Frequency Factors for the Reaction

$$\left[Cr(NH_3)_5Br\right]^{++} + H_2O \longrightarrow \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^-$$

at pH 2.7, 3.7, 4.7 and 5.7

pH	Activation Energy E_a kcal/mole	Frequency Factor Z
2.7	22.0 ± 0.2	$8 \times 10^{13} \pm 3 \times 10^{13}$
3.7	20.1 ± 0.2	$4 \times 10^{12} \pm 2 \times 10^{12}$
4.7	21.0 ± 0.2	$1.7 \times 10^{13} \pm 0.5 \times 10^{13}$
5.7	20.7 ± 0.2	$1.2 \times 10^{13} \pm 0.4 \times 10^{13}$

The variation of rate constant with hydrogen ion concentration is not linear as might be expected[11]. Instead the rate constant appears to have a linear variation with the logarithm of the hydrogen ion concentration. Plots of the rate constant vs. pH at the three temperatures, 0°, 25° and 50° are shown in Figures 7, 8 and 9, respectively.

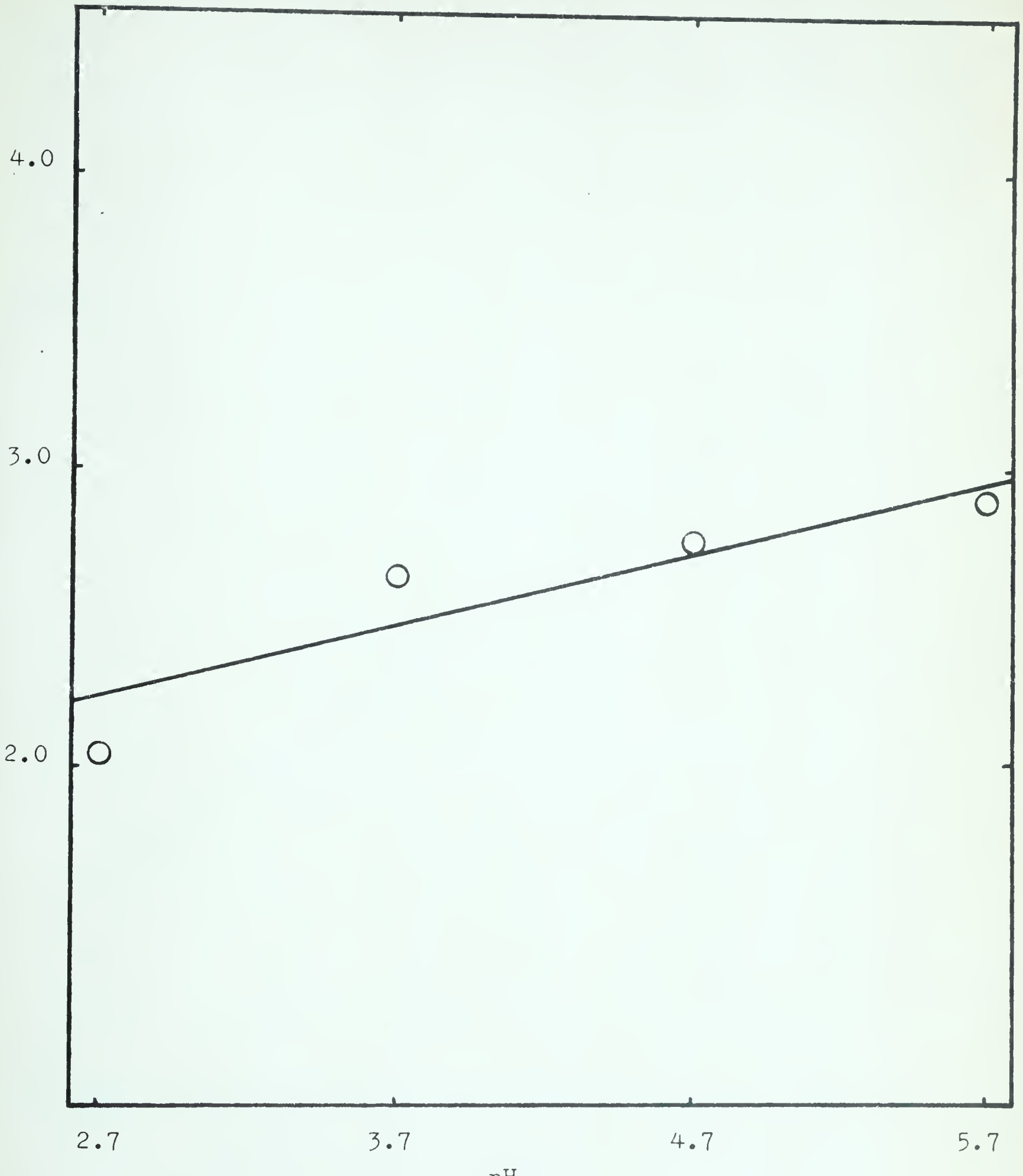


Figure 7 - Variation of first order rate constants at 0°, with pH

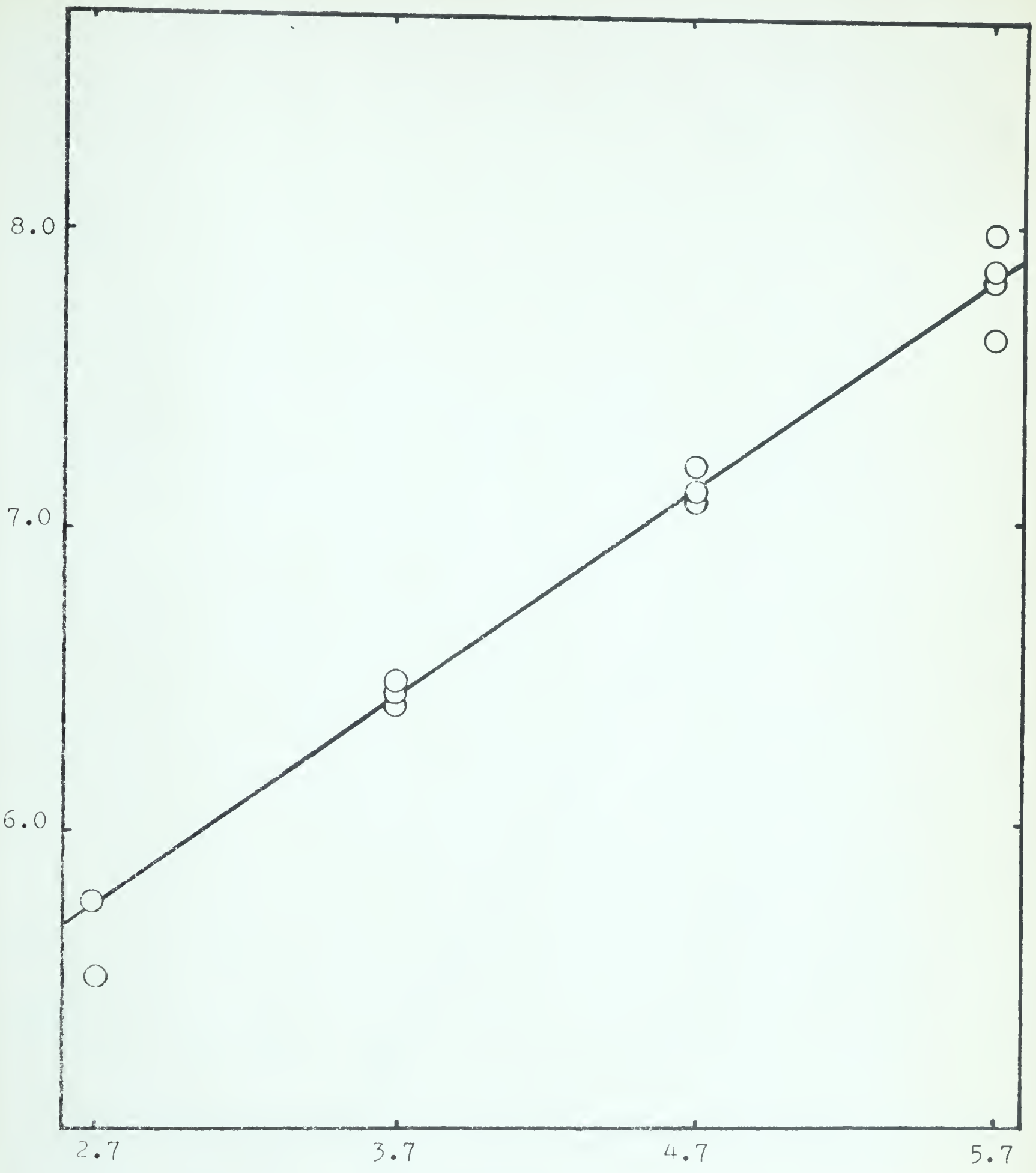


Figure 8 - Variation of first order rate constants at 25° with pH

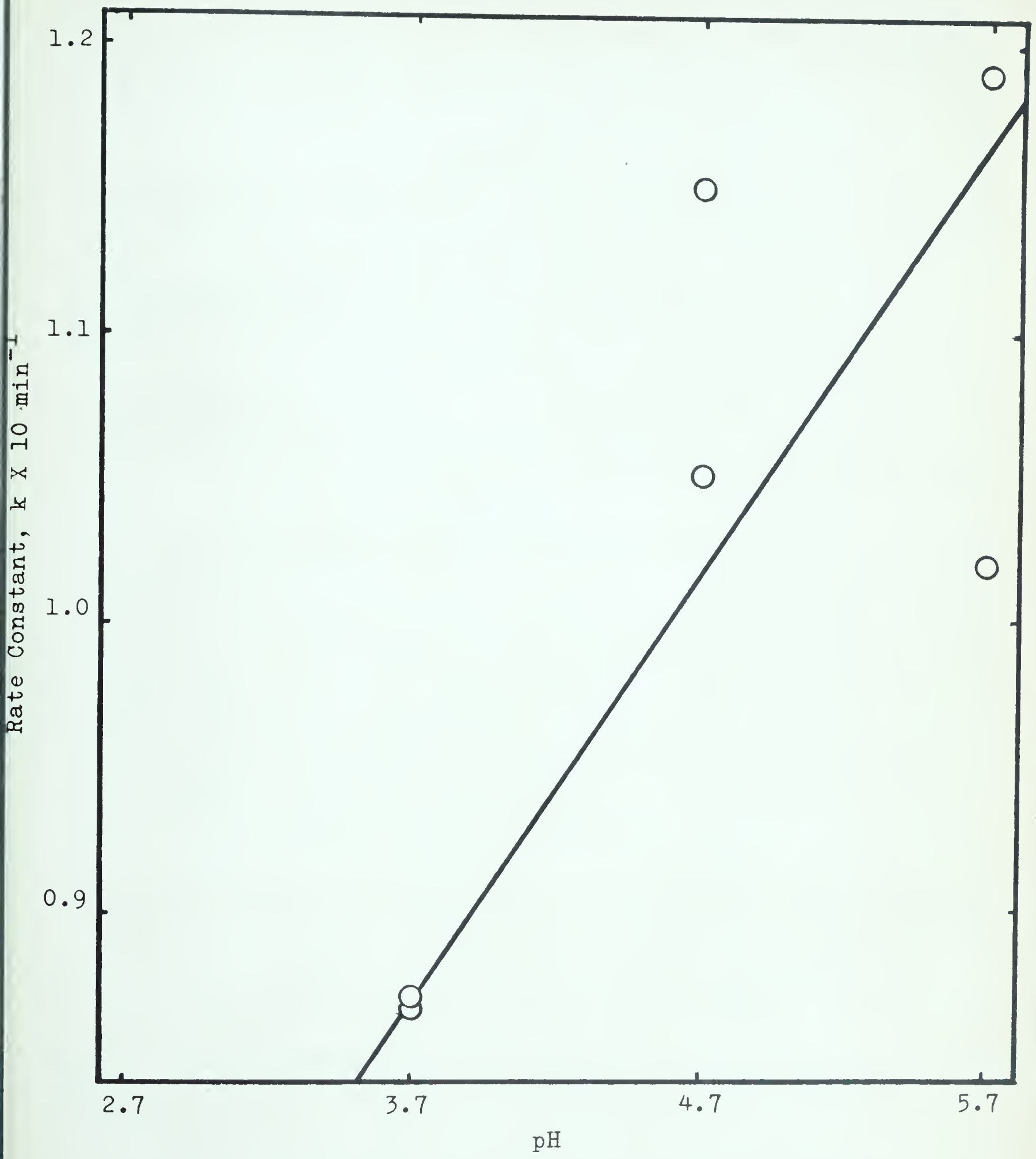


Figure 9 - Variation of first order rate constants at 50°, with pH

To test the effect of acetate ion concentration upon the rate, kinetic determinations were made in buffer solutions which were from 0.01 M to 1.0 M in acetate ion. The results are illustrated in Table V.

TABLE V

The Effect of Acetate Ion Concentration on the Rate Constants at 25° for the Reaction

$$\left[Cr(NH_3)_5Br\right]^{++} + H_2O \longrightarrow \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^-$$

Acetate Ion Concentration	Rate Constants, Min^{-1}	
	pH 3.7	pH 4.7
0.01 M		5.99×10^{-3}
0.1 M ‡	6.44×10^{-3}	7.13×10^{-3}
1.0 M	3.45×10^{-3} 3.22×10^{-3} *	7.67×10^{-3}

* polarograms recorded with no thymol

‡ average values from Table IV.

It is seen from this table that at pH 3.7 an increase in the concentration of the buffer decreases the rate constant, whereas at pH 4.7 the effect of acetate concentration is in the opposite direction. A plot of rate constant for pH 4.7 vs. acetate ion concentration is illustrated in Figure 10.

In order to test the reversibility of the reaction, an excess of sodium bromide was added to the reaction solution. The results are shown in Table VI.

TABLE VI

The Effect of Bromide Ion Concentration on the Rate Constant for the Reaction $\left[Cr(NH_3)_5Br\right]^{++} + H_2O \longrightarrow \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^-$

	Concentration of added NaBr ⊕	Rate Constants min^{-1}		
		pH 3.7	pH 4.7	pH 5.7
25°	∓ 0	6.44×10^{-3}	7.13×10^{-3}	7.81×10^{-3}
	0.01 M			6.30×10^{-3}
	0.1 M	5.75×10^{-3}*	6.20×10^{-3}	6.07×10^{-3}
50°	∓ 0	8.67×10^{-2}	1.10×10^{-1}	1.11×10^{-1}
	0.01 M	1.01×10^{-1}* 1.15×10^{-1}		

* polarograms run with no added thymol

∓ average values from Table IV

⊕ In addition there is a contribution to the total bromide concentrate from the complex ($2X10^{-3}$ at the start of the reaction and $3X10^{-3}$ at the end).

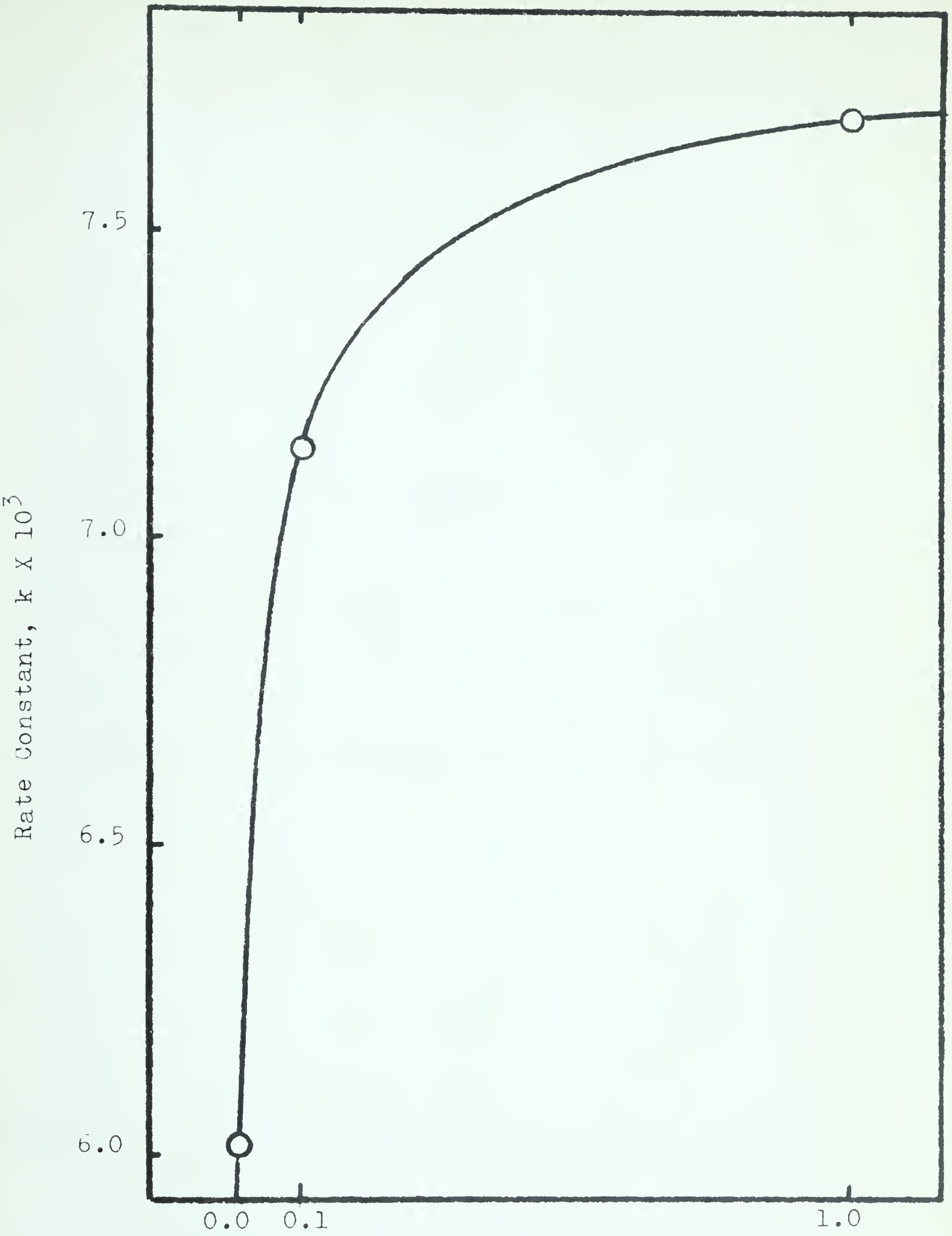


Figure 10 - Effect of concentration of acetate ion on rate constant

It can be seen from this table that the observed rate constant decreases as the bromide ion concentration increases, except at 50° at pH 3.7, where the effect is in the opposite direction. Figure 11 shows plots of the rate constant against the concentration of added bromide.

In order to test the effect of salts upon the rate, the rate constant was determined at pH 3.7 with 1.0 M added potassium nitrate. However, the complex was so slightly soluble in this solution that the diffusion current was very low. Consequently, the relative errors in reading the diffusion current were rather large. For this reason the precision of the measurements were low. The rate constants found in the nitrate solution were 5×10^{-3} min^{-1} and 7×10^{-3} min^{-1}. Since the rate constant without the added potassium nitrate was 6.44×10^{-3} min^{-1}, there was no salt effect within the precision of the measurements.

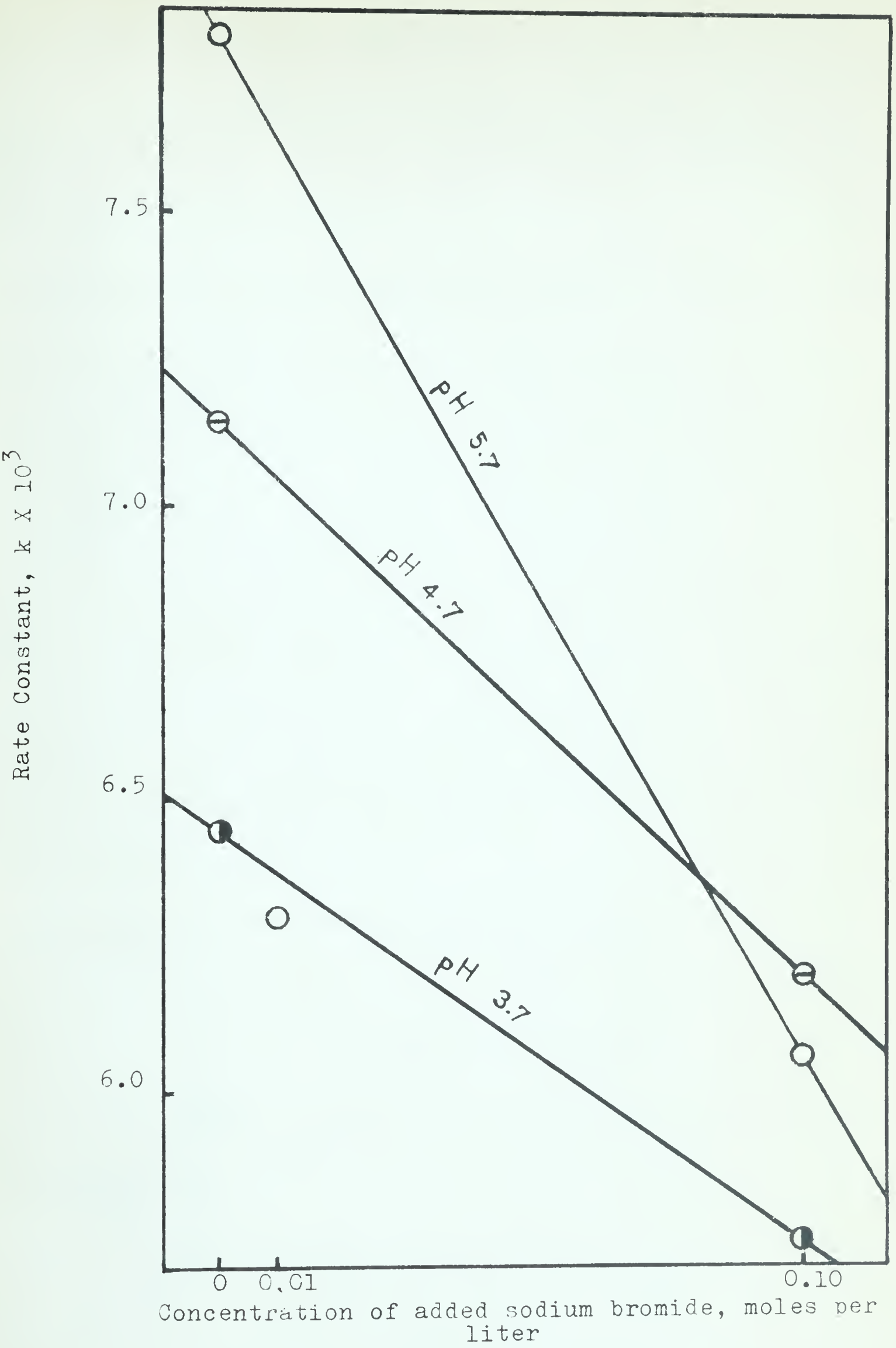


Figure 11 - Effect of concentration of bromide ion on rate constant

DISCUSSION

The displacement of bromide from the bromopentamminechromium (III) ion by water is most simply represented by equation (7).

$$\left[Cr(NH_3)_5Br\right]^{++} + H_2O \xrightarrow{k_1} \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^- \qquad (7)$$

This reaction would follow first order kinetics, and as a consequence agrees with the data presented here for the dependence of rate upon the bromopentamminechromium (III) ion concentration. According to this equation the rate constants at the various pH values should be the same, as there is no hydrogen ion involved. However, a variation in rate constant was found as the pH was changed. Consequently, an additional reaction which is pH dependent must then be considered. Such a reaction is the attack on the bromopentammine by a hydroxide ion. The combined reaction scheme is shown in equation (8).

$$\begin{array}{ccc} \left[Cr(NH_3)_5Br\right]^{++} + H_2O & \xrightarrow{k_1} & \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^- \\ & \searrow^{OH^-}_{k_2} & \downarrow \uparrow H^+ \\ & & \left[Cr(NH_3)_5OH\right]^{++} \end{array} \qquad (8)$$

The rate expression corresponding to this scheme is given in equation (9).

$$\frac{-d[A]}{dt} = [A]\left\{k_2[OH^-] + k_1\right\} \qquad (9)$$

$[A]$ is the concentration of $[Cr(NH_3)_5Br]^{++}$ at any time t , k_1 is the rate constant for the acid hydrolysis step which includes the concentration of water and k_2 is the rate constant for the base hydrolysis step. Therefore:

$$k_t = k_2[OH^-] + k_1$$

where k_t is the overall rate constant

$$[OH^-] = \frac{K_w}{[H^+]}$$

$$k_t = \frac{k_2 K_w}{[H^+]} + k_1 \qquad (10)$$

It can be seen from equation (10) that although the reaction scheme shows a hydrogen ion dependence, it is not the dependence which was observed. In this scheme the overall rate constant would have a linear dependence upon the reciprocal of the hydrogen ion concentration, whereas the observed rate constant shows a linear dependence upon the logarithm of the reciprocal of the hydrogen ion concentration. Therefore, this would be an argument against the reaction scheme illustrated in equation (8), and it is not the only argument against it. There are several reasons why the direct replacement of bromide by hydroxide would seem unlikely. The solvation energies of the bromopentammine and of the hydroxopentammine would be similar due to the fact that both ions have the same charge, and approximately the same size. Also,

the hydroxide ion and the bromide ion have approximately the same nucleophilic character[23], and thus would be bound with roughly equal energies. If the substitution reaction is S_N1 in character the rate is determined primarily by bond breaking. Since the bonding energies are similar, one would expect similar activation energies for the bromo and hydroxo complexes. Hence they would probably also have similar rate constants. With all the above factors roughly equal, the relative concentrations of bromide ion and of hydroxide ion in solution will be the determining factor. For a millimolar solution, with no added bromide, the concentration of bromide ion due to the ionic bromide of bromopentamminechromium (III) bromide is 2×10^{-3} M at the beginning of the reaction and 3×10^{-3} M at the end of the reaction. In the buffer solution of highest pH, 5.7, the hydroxide ion concentration is only 5.5×10^{-9} M. Since the bromide ion concentration is about 10^6 times greater than the hydroxide ion concentration, and since the rate constants are likely to be approximately equal for the forward and reverse reactions, one would hardly expect the forward reaction to take place to any measurable extent. There is another factor which makes it still more unlikely that the attack by hydroxide ion will contribute much to the hydrolysis rate. The nucelophilic character of the water molecule is much greater than that of the hydroxide ion, and with it present in such an overwhelming concentration compared to

the hydroxide ion, attack by water would be very much favoured. Any contribution due to the hydroxide ion should be negligible.

Consequently, another modification of equation (7) must be considered. Such a reaction scheme which would show a pH dependence involves the loss of a proton from an ammine group and subsequent hydrolysis of the conjugate base. This type of reaction path has been considered in the hydrolysis of the chloropentamminecobalt (III) ion, by Pearson, Meeker and Basolo[12], and is illustrated in equation (11) for the chromium pentammine.

$$\begin{array}{ccc} \left[Cr(NH_3)_5Br\right]^{++} & \xrightarrow[k_1]{H_2O} & \left[Cr(NH_3)_5H_2O\right]^{+++} + Br^- \\ \Big\downarrow K \quad \Big\uparrow H^+ & & \Big\downarrow \quad \Big\uparrow H^+ \\ \left[Cr(NH_3)_4(NH_2)Br\right]^{+} & \xrightarrow[k_3]{H_2O} & \left[Cr(NH_3)_4(NH_2)H_2O\right]^{++} + Br^- \end{array} \qquad (11)$$

The effect upon the Cr-Br bond of removing a proton from one of the ammine groups was mentioned in the introduction (cf. p6). This effect should be apparent as an increase in the rate of removal of bromide by an S_N1 path for the reaction. The rate expression which fits the reaction paths illustrated in equation (11) is given by equation (12).

$$\frac{-d[A]}{dt} = k_1[A] + k_3[B] \qquad (12)$$

$[A]$ is the concentration of $\left[Cr(NH_3)_5Br\right]^{++}$, $[B]$ is the con-

centration of the conjugate base $\left[Cr(NH_3)_4(NH_2)Br\right]^+$, k_1 is the rate constant for the hydrolysis of the pentammine bromide and k_2 is the rateconstant for the hydrolysis of the conjugate base. Equation (12) is satisfactory provided the equilibrium set up between the acid and the conjugate base of the bromide is very rapid. It has been shown that this is the case with the corresponding cobalt complexes[12]. Since the K_a values for the acid dissociation of the aquo-pentammine complexes of chromium and cobalt are similar, (for cobalt pK_a is 6.55 and for chromium pK_a is 5.30)[24], one would expect the acid dissociation constants of the halogenopentamminecobalt (III) ion and of the halogenopen-tamminechromium (III) ion to be similarly related. Pearson and Basolo[25] have estimated the acid dissociation constant of the chloropentamminecobalt (III) ion to have a maximum value of 10^{-14}. Therefore, it is expected that the acid dissociation constant for bromopentamminechromium (III) ion would have a maximum value of about 10^{-13}. As a result of the acidity of the solutions in this study and of the very small value for K_a the concentration of the amidobromotetram-minechromium would be extremely small. Consequently, for any significant contribution from the step involving the con-jugate base, k_3 will have to be rather large.

Using the expression $\left[B\right] = \frac{K\left[A\right]}{\left[H^+\right]}$ equation (12)

becomes

$$\frac{-d[A]}{dt} = \left\{ k_1 + \frac{k_3 K}{[H^+]} \right\} [A] \qquad (13)$$

It can be seen from equation (13) that the overall rate constant shows a linear variation with the reciprocal of the hydrogen ion concentration, which was one of the shortcomings of the previous scheme, involving hydroxide ion attack. Using as k, the observed values for the rate constant at pH 3.7, 4.7 and 5.7, k_3K can be calculated, from equation (14) for the two pH intervals.

$$k = k_1 + \frac{k_3 K}{[H^+]} \qquad (14)$$

At pH 3.7 equation (14) becomes

$$6.44 \times 10^{-3} = k_1 + \frac{k_3 K}{1.8 \times 10^{-4}} \qquad (15)$$

and at pH 4.7 equation (14) becomes

$$7.13 \times 10^{-3} = k_1 + \frac{k_3 K}{1.8 \times 10^{-5}} \qquad (16)$$

Subtracting equation (15) from equation (16).

$$.69 \times 10^{-3} = \frac{9 k_3 K \times 10^4}{1.8}$$

Therefore $k_3K = 1.38 \times 10^{-3}$ for the interval between pH 3.7 and pH 4.7. For pH 5.7 equation (14) becomes,

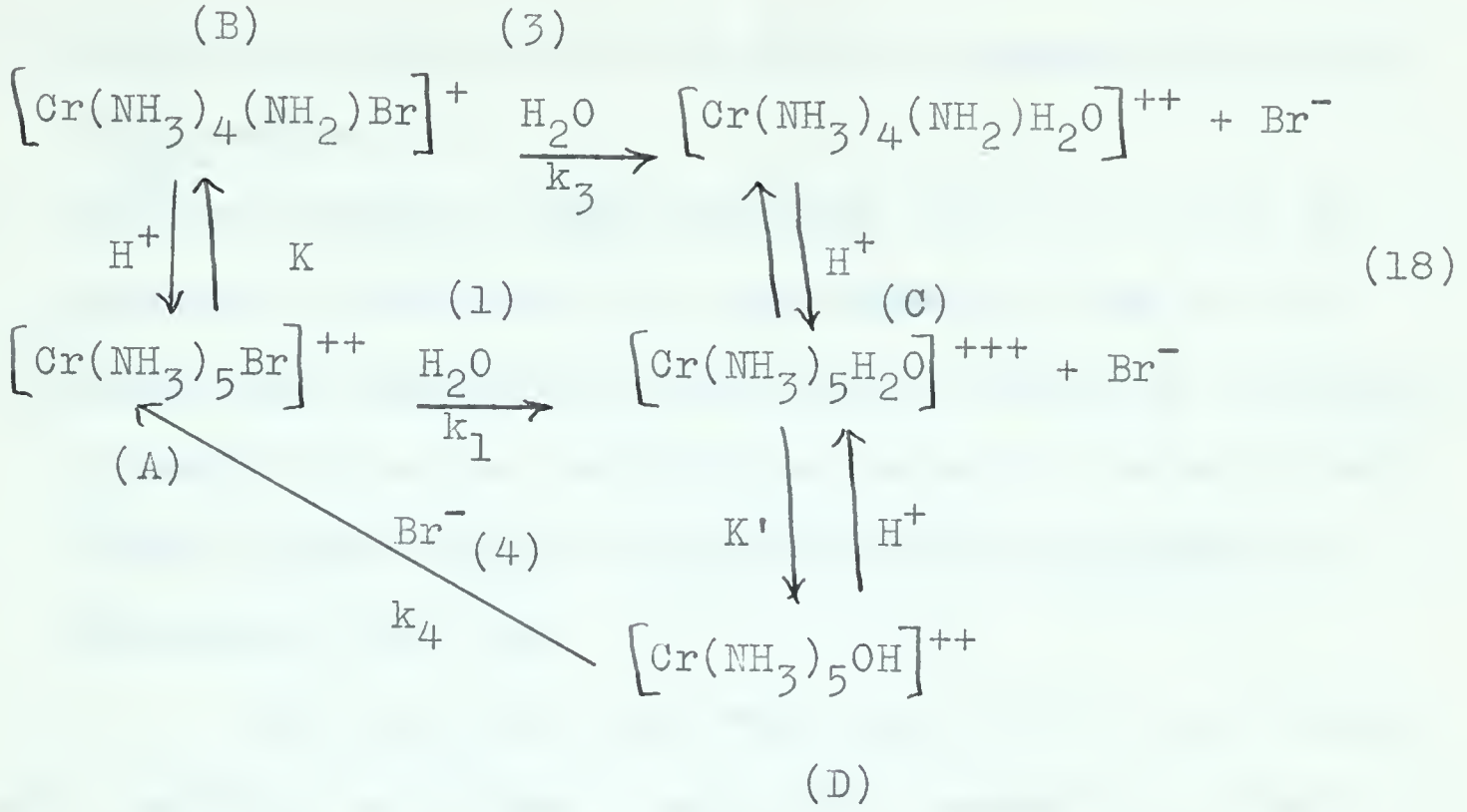
$$7.81 \times 10^{-3} = k_1 + \frac{k_3 K}{1.8 \times 10^{-6}} \qquad (17)$$

Subtracting equation (16) from equation (17)

$$.68 \times 10^{-3} = \frac{9k_3K \times 10^5}{1.8}$$

Therefore $k_3K = 1.36 \times 10^{-9}$ for the interval between pH 4.7 and pH 5.7. If the reaction scheme proposed were valid as it stands, k_3K should be equal for both calculations, which is not the case. In spite of this objection, it has been found that a mechanism of this kind explains many hydrolysis reactions[11,12,26]. Thus it is not permissible to arbitrarily discount this path. Nevertheless, additional reaction paths will have to be considered.

None of the schemes discussed so far shows any bromide dependence. A decrease in the observed rate constant was found when the bromide ion concentration was increased by adding an excess of sodium bromide. This mass law effect is accounted for by proposing an additional step which was the reverse of the reaction which was added in equation (8). This new mechanism illustrated in equation (18) has a reverse step which is hydrogen ion dependent but which operates in the opposite direction to the hydrogen ion dependence of the step involving the conjugate base. These two opposing hydrogen ion dependent terms could combine to produce the observed effect,



In this scheme there are two possible reverse steps, step (4) and the reverse of step (3), which are not kinetically distinguishable. It was concluded previously, that since the forward and reverse rate constants for step (4) would probably be similar, and since the bromide ion concentration far exceeds the hydroxide ion concentration, step (4) is likely to proceed as it is written in equation (18). On the other hand, the reverse of step (3) is improbable for the following reasons:

1. The solvation energy of the dipositive cation would be greater, and this represents an unfavorable enthalpy term for the reverse reaction.
2. Water is a better nucleophile, and hence would be bound in the complex with a greater energy. Because of this, the activation energy for the forward reaction would be less, thus favoring a larger rate constant in this direction.

3. Water is present in a far greater concentration than the bromide ion.
4. The amidoaquotetramminechromium (III) ion would be present in extremely low concentration due to the very large equilibrium constant in favor of a proton transfer from the coordinated water to the more basic amido ligand, thus forming the hydroxopentammine-chromium (III) ion.

Since all the acid base equilibria are obtained very rapidly, and since a negligible amount of chromium is present at any time in the forms amidobromotetrammine-chromium (III), and amidoaquotetramminechromium (III), equation (13) can be combined with a term, given in equation (19) involving the reverse reaction or step (4).

$$\frac{d[A]'}{dt} = k_4[D][Br^-] \qquad (19)$$

$\frac{d[A]'}{dt}$ is the rate of formation of A from D, $[D]$ is the concentration of $[Cr(NH_3)_5OH]^{++}$ and k_4 is the rate constant for this reverse step. Since $[C] = \frac{[H^+][D]}{K'}$ (20)

and $[C] + [D] = [A_o] - [A]$ (21)

where $[A_o]$ is the initial concentration of A, equations (20) and (21) can be combined to give

$$[D]\left\{1 + \frac{[H^+]}{K'}\right\} = [A_o] - [A]$$

$$[D] = \frac{[A_o] - [A]}{1 + [H^+]/K'}$$

Substituting this value of $[D]$ into equation (19) gives

$$\frac{d[A]'}{dt} = \frac{k_4}{1 + [H^+]/K} \left\{ [A_o] - [A] \right\} [Br^-] \qquad (22)$$

Combining equations (13) and (22), equation (23) is obtained.

$$\frac{-d[A]}{dt} = \left\{ k_1 + \frac{k_3 K}{[H^+]} + \frac{k_4 [Br^-]}{1 + [H^+]/K'} \right\} [A] - \frac{k_4 [Br^-]}{1 + [H^+]/K'} [A_o] \qquad (23)$$

For constant hydrogen ion concentration and constant bromide ion concentration, equation (23) can be written as

$$\frac{d[A]}{dt} = n - m[A] \qquad (24)$$

where $m = k_1 + \frac{k_3 K}{[H^+]} + \frac{k_4 [Br^-]}{1 + [H^+]/K'}$

and $n = \frac{k_4 [Br^-]}{1 + [H^+]/K'} [A_o]$

Integrating between the limits 0 to t and $[A_o]$ to $[A]$, equation (24) becomes

$$t = \frac{1}{m} \; 2.303 \log \left\{ \frac{n - m[A_o]}{n - m[A]} \right\} \qquad (25)$$

For this equation to have meaning both $m[A_o]$ and $m[A]$ must be larger than n.

The integrated form, equation (25), is valid only if the bromide and hydrogen ion concentrations are constant. Therefore, the constants n and m were calculated using experimental values of $[A]$ and t obtained from the study of solutions which were at pH 5.7 and 0.1 M in sodium bromide. In this study when t = 100 minutes, $[A] = 3.2 \times 10^{-7}$ M and when t = 200 minutes, $[A] = 1.8 \times 10^{-4}$ M. Substituting these values into equation (25) the following simultaneous equations were obtained:

$$100 = \frac{1}{m} \; 2.303 \log \left\{ \frac{n - 10^{-3} m}{n - 3.2 \times 10^{-4} m} \right\} \qquad (26)$$

$$200 = \frac{1}{m} \; 2.303 \log \left\{ \frac{n - 10^{-3} m}{n - 1.8 \times 10^{-4} m} \right\} \qquad (27)$$

Substituting various values for m, the corresponding values of n were calculated, from each equation. Then log n was plotted against the corresponding values of m, forming two intersecting lines. The values of n and m at the point of intersection were the solution to equations (26) and (27). However, when the values of n and m, obtained in this way, were tested using other values of t, equation (25) did not yield the observed values of $[A]$. Hence although the reaction scheme proposed, agrees qualitatively with the data presented here, it does not agree quantitatively.

Although the specific reaction scheme proposed cannot be quantitatively substantiated with the present data,

certain conclusions regarding the mechanism of reaction can be made. One such conclusion is based upon the relative activation energies of the possible transition states. It was mentioned in the introduction (cf. p. 5) that the seven coordinated transition state and the five coordinated trigonal bipyramid transition state have estimated activation energies of 103 kcal[10] and 121 kcal[10] respectively for cobalt complexes and would probably have similar values for chromium complexes. These are much too high to be consistent with the data presented here. The experimental activation energy of 20-30 kcal would, however, be consistent with a square pyramid transition state, for the activation energy of this probably has a similar range as that for cobalt complexes, which is 6-94 kcals[10]. Therefore, it would seem that the most favorable path involves the dissociation of the leaving group (S_N1 mechanism) but in order for the activation energy to be of the right order of magnitude it must be an assisted dissociation. Such assistance can result from participation of a water molecule, so as to partially occupy the vacated position, thus preventing the molecule from collapsing into a new configuration.

It can also be seen that considerations of the relative rates of hydrolysis of the halogenopentammine-chromium (III) ions is more consistent with an S_N1 mechanism. If the reaction proceeds by a cis S_N2 limiting mechanism

the rate ought to decrease with an increase in size of the displaced group. The larger the leaving group, the less room is available for a cis attack of the nucleophile. Thus the chloride complex ought to react faster than the bromide complex which ought to react faster than the iodide. For an S_N2 trans attack, both ordinary and limiting, there should be no change in rate with a change in the size of the leaving group. On the other hand, for an S_N1 mechanism increasing size of the leaving group ought to result in an increased rate of reaction, due to a straining of the bonds. Freundlich and Bartels found the rate constant for the chloropentamminechromium (III) ion to be 5×10^{-4} min^{-1} at 25°[14], and for the iodopentamminechromium (III) ion to be 10^{-2} min^{-1} at 0°[14] which means it would likely be much larger at 25°. In the present study the average rate constant for the bromopentamminechromium (III) bromide was found to be about 7×10^{-3} min^{-1}. The large rise in the rate constant with increasing size of the leaving group is indicative of an S_N1 mechanism.

Another factor favoring an S_N1 mechanism is the fact that the rate constant was found to increase with increasing concentration of the acetate ion. By increasing the acetate ion concentration, there would be an increasing number of acetate ions associated with the ammine ligands, by hydrogen bonding. The resulting increased crowding about the ion would inhibit the attack of a nucleophile and would

be unfavorable to a seven coordinated transition state. Hence the rate constant for a reaction proceeding by an S_N2 mechanism would decrease with an increasing concentration of the acetate ion. On the other hand, the association of the acetate ion with the complex would increase the charge density about the central chromium ion, thus favoring a unimolecular bond rupture[27]. Therefore, the rate constant for a reaction proceeding by an S_N1 path would increase with an increasing concentration of the acetate ion, which is the trend which was found. One apparent inconsistency, is that at pH 3.7 an increase in the concentration of the acetate ion resulted in a decrease in the rate constant. In this case it should be pointed out that at this pH, when the acetate ion concentration is one molar, the concentration of the acetic acid is ten molar. With this large concentration of acetic acid, there is only five times as much water as acetic acid in solution, and thus there would be appreciable competition between the bromopentammine and the acetic acid, for the available water molecules. Hence it seems reasonable that there should be a decrease in the rate constant.

In summary the above evidence seems to indicate that the substitution reaction is predominately S_N1 in character.

The path proposed for the forward reaction via the amido intermediates, step (3), equation (18), could

only be correct if the reaction proceeds by an S_N1 mechanism (cf. p. 41). Also, the argument in favour of the reverse reaction, step (4), equation (18) is only valid if it also is S_N1 in character (cf. p. 40). More data has to be obtained, especially on the bromide ion dependence of the rate constant before any of the reaction paths proposed in equation (18) can be quantitatively substantiated. If, however, the reactions proceeding by the amido intermediates, step (3), and the reverse reaction, step (4), are correct this would be further evidence in favour of an S_N1 mechanism.

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